The present invention relates to cellulose base lubricating grease, that is, lubricating grease wherein cellulose, or cellulose derivatives, are employed as the thickening or gel forming material which forms the grease structure.

The present application is a continuation-in-part of our copending applications, Serial No. 66,130 and Serial No. 68,153, filed December 18, 1948, now Patents No. 2,583,603 and 2,583,606, issued January 29, 1952.

In the above-mentioned applications, lubricating greases and processes for their preparation are described where the normal solvent or liquid component which is present in a gel or related material, such as water, is replaced first with a mutual solvent for oil and water and finally the mutual solvent is replaced, directly or indirectly, by a lubricating oil. Greases of this type have some very desirable properties. They appear to have certain advantages over soap thickened greases of conventional type, some of them being especially suited for high temperature service. However, as also pointed out in the aforesaid applications, these greases commonly have the disadvantage that water tends to replace the oil upon contact, causing the composition to break down when moisture gains access to the lubricant.

During the course of experiments relating to the present invention it has been found that the oil thickeners useful for grease making must have certain physical properties. Conventional colloidal suspensions of grease forming particles, such as the soaps of prior art lubricating greases, usually must have a high ratio of length to breadth if they are to be useful. In other words, the soap fibre which forms in a lubricating grease for giving it structural stability are relatively long, slender and essentially fibrous in character.

Various materials other than soaps have been found in the prior art to have gel forming characteristics, with lubricating oil. In general, however, the shape of the particles, as well as their size, has an important bearing upon the character and stability of the lubricating grease. It appears that the solid phase of a lubricating grease should not only be fibrous, and its particles relatively long and slender, but it should also possess a strong affinity for oil so that it will attract and hold the lubricating oil to its surfaces to give the grease structural stability. Patent No. 2,583,603, mentioned above, points out how various materials much unlike conventional soaps, such as wood pulp and other cellulose substances may be divided into micro-particles sufficiently fine that a good grease structure may be established when they are placed in oil.

It is therefore an object of the present invention to prepare stable lubricating greases from cellulose and cellulose type materials while at the same time avoiding the objectionable instability of such greases in the presence of moisture. According to the present invention, the addition of certain resins and/or metal soaps to the cellulose materials tends to render them relatively water repellent. Such treatment of the cellulose material is an important feature of the present invention.

When the normal water content of cellulose is replaced by acetone, for example, and the acetone ultimately replaced by mixing with a lubricating oil such as mineral base oil, and then flashing off the acetone, the cellulose retains its original colloidal or gel like structure unless and until it comes in contact with moisture. The lubricant is relatively useless in the presence of moisture, however, without additional treatment. By treating the cellulose, while in the presence of oil, with surface active agents which are hydrophobic in nature, the greases are very substantially improved. Various materials which reduce substantially the preferential adsorption of water on cellulose and which are sufficiently oleophilic to be wetted by oil may be employed to accomplish the desired result. The oil soluble water insoluble resins and soaps are preferred.

A particularly suitable surface active agent is the resinous reaction product of substantially equimolar proportions of maleic anhydride and glyceryl monoricinoleate. Other resins of similar type may be used.

A further feature of the present invention involves the treatment of the cellulose itself to give it the desired physical properties for preparation of lubricating greases. Cellulose of appropriate type may be readily obtained by treating viscose with dilute mineral acids such as sulfuric acid or phosphoric acid. The sulfuric acid treatment is normally preferred. By carrying out the acid precipitation in the presence of sodium sulfate cellulose is produced of sufficiently fine fibrous structure that it sets up a stable grease structure with lubricating oils. On the other hand if the cellulose is precipitated without treatment with sodium sulfate the fibrous structure of the precipitated cellulose is somewhat coarser and less satisfactory.

Although the resins reaction product of maleic anhydride and glyceryl monoricinoleate is a
preferred surface active agent, to render the grease water repellant and physically stable, other types of surface active agents may be used. In particular, the relatively oil soluble and water insoluble long chain fatty acid soaps of certain metals may be used to treat the cellulose before oil is incorporated therein. In general, these metal soaps which make good grease thickening agents but which are substantially insoluble in water, such as aluminium, calcium, barium, or lithium stearate and related materials are useful. It is preferred that they be used in proportions of about 3 to 60% by weight based on the weight of solvent exchanged cellulose treated therewith, or about one-tenth of these quantities based on the total grease. It is preferred, however, to use at least some resin of the type mentioned above, using soap along with the resin where the soap can otherwise be tolerated. Thus a composition containing about 4 to 10% by weight of cellulose, based on the solvent-free material, about 4 to 8% of the maleic anhydride-glyceryl mono ricinoleate resin, 0 to 6% of soap, and the remainder of lubricating oil, preferably but not necessarily of mineral base, makes a good grease composition. Cellulose which has not been treated with soap at all can be used.

When soap treated cellulose is to be used, the soap is preferably formed on the cellulose as the latter is precipitated. In either case, upon precipitation a slurry of viscoso is formed which may be treated next with a mild alkaline solution to condition it for further processing. Thereafter the slurry is filtered and the precipitated cellulose is washed substantially free from water soluble materials. It is next solvent exchanged with a soluble mutual solvent for oil and water, such as acetone. Other mutual solvents, such as an appropriate alcohol or ether, especially propyl and butyl alcohols, and pyridine, may be used in lieu of acetone, some of these being pointed out in Patent No. 2,583,693 previously mentioned. The solvent selected should vaporize at a temperature well below that of the microcrystalline oil or other lubricating oil used. The mutual solvent may, in turn, be replaced directly by lubricating oil or it may first be replaced by an intermediate solvent such as petroleum ether or the like and the latter replaced by the lubricating oil. In this way, the water of the cellulose-water system may be removed without shrinkage of the cellulose. The cellulose-solvent system thus obtained may be termed a solvent-exchanged cellulose. Greases made directly from this type of cellulose, i.e. by solvent exchange, result when oil is added to the solvent-exchanged cellulose and the solvent is flashed off. They immediately begin to disintegrate, however, in the presence of water. The cellulose component absorbs or adsorbs water in preference to oil and the product is useless, especially where the grease is to come in contact with free water or with appreciable quantities of moisture in any form.

The grease of this invention may be substantially improved in water resistance by adding modified resinos condensation products of polyhydric alcohol and polybasic acid. These may be water-prooiling agents of the malic-glycerol ester type, previously mentioned. The manner in which this is done is an important aspect of this invention. While, as previously mentioned, the preferred waterprooiling agent is the reaction product of maleic anhydride and glycerol monoricinoleate in substantially equimolar proportions, related alkyl resins such as those obtained by reacting tetrachlorophthalic anhydride with glycerylmonooleate in substantially equimolar proportions, related monooesters of glycerol, such as the mono-oleate or monoricinoleate may be used. In order to test water repellancy of various grease samples an apparatus was devised consisting of an elongated grease worker of 50 cc. capacity fitted with a single orifice of 0.04" diameter. For this test about 15 grams of the grease and 40 cc. of water are placed in the worker and forced back and forth through the orifice. This test ordinarily is carried out for 50 cycles, passing the grease and water 100 times through the orifice. Greases which do not liquefy or disintegrate during such tests are considered to be satisfactorily water repellent. Some of the products ran considerably more than 50 cycles which is considered very superior performance. A typical example for obtaining a cellulose in sufficiently finely divided form from viscoso consisted in diluting 500 grams of viscoso with 1500 cc. of water containing 20 grams of sodium sulfate. The cellulose was then precipitated from the solution with the calculated amount of sulfuric acid, diluted with water to a volume of 500 cc. This product was washed free of water soluble salts and solvent exchanged with acetone and the acetone replaced with oil to make a grease in the manner described above. Some samples were tested without addition of waterproofing or surface active agents. In others the maleic anhydride-glyceryl mono ricinoleate resin was added shown in the examples below. In each case, the oil-cellulose system was homogenized to make a grease structure.

**Example I**

6.75% by weight of cellulose based on the weight of the final grease was solvent exchanged first with acetone then with lubricating oil of 200 viscosity S. S. U. at 100° F. The resulting final viscosity index of 95. 95.25% by weight of oil with the cellulose made a grease of good yield value upon homogenization. The product, however, disintegrated without shearing in the presence of water.

**Example II**

5.5% by weight of solvent exchanged cellulose, based on the weight of the final grease composition, prepared as described above, was combined with 5.5% of the resin derived by reacting to completion substantially equimolar proportions of maleic anhydride and glycerol monoricinoleate. To this was added 88.5% of the same mineral oil as in Example I. The resulting grease product had a good consistency and passed the water resistance test of 50 strokes of the plunger in the grease worker test apparatus described above.

**Example III**

6.2% by weight of cellulose, prepared as above, was solvent exchanged, added to 5.4% of maleic anhydride-glyceryl monoricinoleate mixed in 88.5% of oil of 500 S. S. U. viscosity at 100° F., the oil having a viscosity index of 95. A grease of good yield resulted and the product passed the water resistance test in the grease worker very well, being stable and undiluted after 60 strokes of the plunger of the test apparatus.
beneficial. Thus, if a soap such as aluminum stearate is distributed along the active centers of the cellulose fibers to render them somewhat water repellent which may be accomplished by coprecipitating the aluminum stearate with the cellulose, the grease is materially improved. The amount of soap used may be varied as indicated above. This is illustrated in the next examples. The soaps of baryum, calcium and lithium may be substituted, if desired, for aluminum soap. In these cases acetate or chloride ions should be used as precipitating agents instead of sulfate ions.

Example IV

500 grams of viscose were added to 1500 cc. of water containing 20 grams of sodium sulfate and 8.2 grams of sodium stearate. In order to keep the viscosity low the mixture was heated moderately to a temperature of 50 to 60° C. The cellulose and an aluminum stearate were coprecipitated from the solution by adding 500 cc. of an aqueous solution containing the calculated amount of concentrated sulfuric acid and aluminum sulfate. The aluminum sulfate obviously reacts by double decomposition with the sodium stearate to precipitate the aluminum soap. However, since the viscose is normally sufficiently alkaline, stearic acid may be used if desired as an lieu of sodium stearate, e. g. as an emulsion in the first water solution mentioned above.

After precipitation, the slurry of cellulose and soap in water was treated with 5 to 10 cc. of 3 normal ammonium hydroxide. This raised the pH value of the slurry to about 8. The slurry was then filtered, washed free from soluble salts and solvent exchanged with acetone. Oil was added and the acetone flashed off by heating above its boiling point.

Greases made in the manner just described were found to be somewhat water repellent without the addition of resin. However, they disintegrated after shearing in the presence of water at 70° C. and a few strokes in the grease worker described above.

Example V

A cellulose grease was prepared by taking 8.12% of cellulose containing 20% by weight of aluminum stearate and prepared as in Example IV. To this was added 7.08% of maleic anhydride-glyceryl monoricinoleate resin and 84.8% of mineral lubricating oil of 90 viscosity index and a viscosity of 300 S. S. U. at 100° F. The product was of good consistency and good thixotropic properties. It passed the water resistance test of 150 cycles.

Example VI

A grease was prepared as in Example V except that the cellulose contained 10% of its own weight of aluminum mono-stearate. The cellulose and aluminum soap constituted 7.9% by weight, with waterproofing resin 5.4%, and mineral oil of 90 viscosity index and 500 S. S. U. viscosity at 30° F. constituted 88.7%. This product had a good yield value and passed the water resistance test of 150 cycles. It was an excellent grease.

Example VII

A cellulose prepared as in Example IV but containing 3% of its own weight of aluminum mono-stearate coprecipitated therewith was used in proportions of 9.89% by weight, based on the final grease. 5.21% by weight of resin and 86.1% of the same oil as in Example VI were blended together. After flashing off the solvent and homogenizing the product in a colloid mill this grease had a good yield value. It passed the water resistance test of 35 cycles of the plunger but emulsified after 60 cycles. This appears to indicate that it is desirable to have a minimum of at least 3% of the soap in the cellulose and preferably a little more.

Example VIII

8% by weight, based on the final grease composition, of soap coated cellulose, (coprecipitated with 60% of its own weight of aluminum mono-stearate) was prepared as in Example IV. The cellulose was combined with 6% by weight of the resin of Example II and 58% by weight of mineral lubricating oil of 95 viscosity index and 300 S. S. U. viscosity at 100° F. After heating to 125° C. to flash off the solvent, which was used to displace water from the cellulose, the product was passed twice through a colloid mill. The resulting grease was found to possess a very good yield value. It had a very firm consistency, considering the amount of thicker employed. This product also passed the water resistance test of 150 cycles of the plunger.

Instead of the particular maleic anhydride-fatty acid resin described above, other resins, particularly the commercially available alkyl resins modified by treatment with linseed oil may be used as waterproofing agents. The synthetic lubricating oils such as the dibasic acid esters and the polycyclic alcohol derivatives of lubricating oil consistency may be substituted for mineral oil in whole or in part. Also, conventional additives and modifiers such as anti-oxidants, thickening agents, viscosity index improvers, extreme pressure agents and metal deactivators, etc., may be employed in the usual proportions as is known in the art.

What is claimed is:

1. A lubricating grease composition comprising a lubricating oil thickened to a grease consistency with solvent-exchanged cellulose precipitated from viscose containing 3 to 60% by weight, based on the cellulose, of a water insoluble metal soap as a waterproofing agent, said grease containing 2 to 10% by weight, based on the weight of the total composition, of a waterproofing alkyl resin of the glyceral partial ester dibasic acid type.

2. A lubricating grease composition comprising a major proportion of mineral base lubricating oil, 2 to 10% by weight, based on the total grease composition, of solvent exchanged cellulose of gel type precipitated from viscose containing 3 to 60% of its own weight of an aluminum mono-stearate as a hydrophobic agent, and 2 to 10% by weight, based on the total composition of a maleic anhydride-glyceryl monoricinoleate ester resin as a waterproofing agent.

3. Composition according to claim 2 where the amount of resin is between 5 and 8%.

4. Composition according to claim 2 wherein the amount of cellulose is between 5 and 8% of the weight of the total composition.

5. The process of preparing a lubricating grease which comprises coprecipitating a cellulose gel type from viscose with a metal soap capable of rendering the cellulose relatively hydrophobic, adding lubricating oil by solvent exchange to replace the normal water content of the cellulose, incorporating 2 to 10% by weight, based on the total grease composition, of a waterproof-
ing resin, and homogenizing to form a stable grease structure.

6. The process which comprises forming a water slurry of viscose containing minor quantities of sodium sulfate and water soluble C12 to C18 fatty acid radical, coprecipitating the cellulose and the fatty acid radical from said solution by addition of an aqueous solution of a mineral acid and a metal salt of relatively low molecular weight, treating the coprecipitated slurry with a small amount of alkaline material, filtering, washing free from water soluble materials, exchanging the water content of the filtered cellulose with a mutual solvent, for water and oil, replacing the mutual solvent with lubricating oil, adding 2 to 10% by weight, based on the total composition of a waterproofing resin, and homogenizing to form a stable lubricating grease.

7. The process according to claim 6 wherein the lubricating oil is mineral base lubricating oil.

8. The process according to claim 6 wherein the grease contains 2 to 10% by weight of cellulose which in turn contains 3 to 60% of its own weight of a metal soap of long chain fatty acid of the C12 to C18 range said soap being selected from the group consisting of the soap of aluminum, barium, calcium and lithium, as a hydrophobic agent.

References Cited in the file of this patent

UNITED STATES PATENTS

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<thead>
<tr>
<th>Number</th>
<th>Name</th>
<th>Date</th>
</tr>
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<tbody>
<tr>
<td>2,260,625</td>
<td>Kistler</td>
<td>Oct. 28, 1941</td>
</tr>
<tr>
<td>2,573,650</td>
<td>Peterson</td>
<td>Oct. 30, 1951</td>
</tr>
<tr>
<td>2,583,605</td>
<td>Sirianni et al.</td>
<td>Jan. 29, 1952</td>
</tr>
</tbody>
</table>